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Intrinsic luminescence in oriented BeO crystals under VUV and inner-shell excitation

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Abstract

Beryllium oxide (BeO) crystals were investigated by time-resolved low temperature VUV-spectroscopy at the SUPERLUMI station and BW3 beam line of HASYLAB (DESY, Hamburg). Photoluminescence spectra (3–10.5 eV), luminescence decay kinetics upon selective photoexcitation, as well as luminescence excitation (50–650 eV) and reflectivity (9–35 eV) spectra were measured and analyzed for oriented BeO crystals. It was shown that study of oriented crystals makes the traditional time-resolved spectroscopy method essentially more informative. Formation of the self-trapped exciton excited states of different multiplicity was found to sensitively depend on excitation energy and mutual orientation of the crystal's **C** optical axis and electric vector **E** of exciting polarized synchrotron radiation.

Keywords: Synchrotron radiation; Time-resolved spectroscopy; Self-trapped exciton; Luminescence; Inner-shell excitation

1. Introduction

Self-trapped excitons (STE) in wide-gap oxide crystals have been studied during at least for thirty years. However, there is no common opinion about the mechanism of excited state formation and the models of STE in oxides though a methodological approach exists, being successfully developed for such investigations in alkali halides (AH) and alkali earth fluorides. It is firmly established that contrary to AH crystals the self-trapping of excitons occurs only in low symmetry oxides, for example, in SiO_2, α-Al_2O_3, Y_2O_3 crystals (Lushchik, 1985). As a rule, near edge excitonic structure in the spectra of optical constants for these crystals is weakly pronounced or entirely absent. As a consequence, the luminescence excitation spectra in the fundamental absorption edge provide limited information for analysis of the mechanisms of STE excited states formation. Beryllium oxide (BeO) single crystal is the sole low symmetry oxide where the coexistence of free and self-trapped excitons have been established (Ivanov et al., 1988). BeO crystals have a hexagonal structure of the wurtzite type and the widest band gap (E_g=10.63 eV) among oxides. The local tetrahedrons of the crystal structure are distorted along the **C** optical axis. As a result, the axial position (more distant from a cation) of oxygen ion and three radial positions (with an equal distance from a cation) can be identified for each local tetrahedron. The broad bands of the UV- and VUV-intrinsic luminescence were attributed (Ivanov et al., 1994) to the radiative decay of STE of two types. STE1 (peaked at 6.7 eV) and STE2 (4.90 eV) differ in the configuration of a hole nucleus, i.e., a small radius polaron of the O^--ion type localized on the axial (STE1) or on the radial (STE2) anions. A sharp edge excitonic structure in the reflection spectra depends on the mutual orientation of the **C** optical crystal axis and electric vector **E** of exciting polarized synchrotron radiation (SR) as shown in (Feldbach et al., 1992). The purpose of the present work is to obtain new data about the structure and channels of the STE formation in BeO crystals taking advantage of oriented crystals, which add significantly more information to the traditional time-resolved spectroscopy.

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2. Experimental details

BeO crystals have been grown from solution in sodium tungstate melt by the method proposed by Maslov et al. (1980). The impurity content in samples was analyzed using laser mass spectrography and did not exceed 140 ppm Na, 10 ppm Li, 70 ppm Mg, 7 ppm Zn, 16 ppm B, and 2 ppm Al. The single crystal in a form of prism with natural growth faces was studied. The spectra recorded from the same growth face in the orientations $\mathbf{E}\|\mathbf{C}$ and $\mathbf{E} \perp \mathbf{C}$ were compared.

Time-resolved photoluminescence spectra (3–10.5 eV) upon selective photoexcitation, luminescence excitation spectra (50–650 eV), photoluminescence decay kinetics (1–500 ns), as well as reflectivity spectra (9–35 eV) of oriented BeO crystals were measured at the SUPERLUMI station (Zimmerer, 1991) and the BW3 beam line equipped with a luminescence setup (Kirm et al., 2003) of HASYLAB. To investigate the time evolution of the luminescence and its excitation the spectra were measured in time windows with the width Δt_i and the delay time δt_i after an exciting SR pulse. Excitation spectra were corrected for the equal number of incident photons, but emission spectra are presented as recorded without any corrections. The parameters of the decay kinetics were determined by the convolution integral method. The reflection spectra (the angle of incidence of SR was 17.5°) were recorded simultaneously with the luminescence excitation spectra in the fast time window ($\Delta t_1 = 22.5$ ns, $\delta t_1 = 2.0$ ns) to exclude contribution of the slow luminescence.

3. Results and discussion

The low temperature VUV-luminescence of BeO crystals is characterized by the invariable spectral parameters (maximum at 6.7 eV, FWHM = 0.8 eV) for any type and energy of excitation producing either excitons or electron-hole pairs (Ivanov et al., 1994). No orientation-related effects were revealed for the VUV-luminescence in the present work. The decay kinetics of the 6.7 eV luminescence at $T = 6$ K is composed of two exponential components (190 and 850 μs), which points to the triplet character of the STE1 excited states. These components are caused by transitions from the different spin sublevels of the split triplet state (Ivanov et al., 1994). In reduced bunch mode of SR the temporal possibilities of used equipment for the decay kinetic analysis are limited by a time range of 1–500 ns. Therefore, the VUV-luminescence spectra, as well as the 6.7 eV luminescence excitation spectra measured in the different time windows coincide.

In contrary, the UV-luminescence spectrum at $T = 10$ K essentially depends on orientation as well as on the energy of incident photons (Figs. 1 and 3). In the kinetics of the UV-luminescence the components with decay times of 30 ns and 10 μs were obtained earlier (Ivanov et al., 1994). At the $\mathbf{E}\|\mathbf{C}$ orientation and the energy of incident photons equal to 10.25 eV the UV-luminescence spectra measured in the fast and slow time windows differ insignificantly (Fig. 1). Taking into account the spectral position of the first maximum of the excitonic reflection at this orientation (∼ 10.43 eV) we concluded that in this case the emission of impurities or defects was excited. A gradual increase in the energy of exciting SR in the range of the fundamental absorption bands leads to essential difference between UV-luminescence spectra measured in fast (maximum at 4.0 eV, FWHM = 1.0 eV) and in slow (maximum at 4.7 eV) time windows (Fig. 1). At least three exponential components (2.2, 54 and > 500 ns) were obtained in the decay kinetics of UV-luminescence in a range of 10.2–10.7 eV of exciting SR energies. The fast UV-luminescence with the maximum at 4.0 eV and an exponential decay time of 2.0 ns was recorded earlier by Pustovarov et al. (1994) under hard X-ray SR excitation (3–62 keV) only for the $\mathbf{E}\|\mathbf{C}$ orientation. At the same time several slower components (29 ns and μs-range) were registered by Ivanov et al. (1994) at the excitation with 6 keV electron beam.

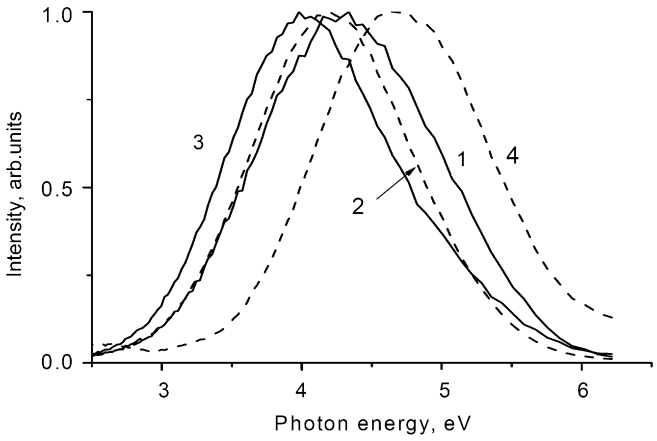

Fig. 1. Time-resolved photoluminescence spectra of BeO crystals ($T = 10$ K) for the crystal orientation $\mathbf{E}\|\mathbf{C}$ at excitation energies of (1, 2) 10.25 eV and (3, 4) 10.7 eV measured in (1, 3) fast ($\Delta t_1 = 2.2$ ns and $\delta t_1 = 8.2$ ns) and (2, 4) slow ($\Delta t_2 = 23$ ns and $\delta t_2 = 111$ ns) time windows.

At $\mathbf{E}\|\mathbf{C}$ orientation the fast and slow components of the kinetic of UV-luminescence decay differ not only in their spectral position, but also in the near edge excitation spectra, as well (Fig. 2). The fast UV-luminescence component (4.0 eV) is most effectively excited in the range corresponding to the $E_{n=2}$ and $E_{n=3}$ maxima of excitonic reflection. In contrary, the range of the most effective excitation of the slow component is immediately adjacent to the energy of $E_{n=1}$. It should be noted that the excitation spectrum of VUV-luminescence (6.7 eV) is similar to that of the fast component of UV-luminescence.

At the alternative orientation ($\mathbf{E} \perp \mathbf{C}$) the intrinsic UV-luminescence of BeO crystals at $T = 10$ K has the spectral maximum at 4.5 eV and slow decay components (55 and > 500 ns) (see Fig. 3). The excitation spectrum of UV-luminescence measured in the slow time window differs from that of the VUV-luminescence (Fig. 4). The UV-luminescence in this case most effectively excited in the $E_{n=2}$ and $E_{n=3}$ energy range, but 6.7 eV luminescence in the $E_{n=1}$ region. It should be pointed out that even in the $E_{n=1}$ range, where the UV-luminescence is effectively excited, both emission bands have different maxima.

The results of the present time-resolved spectroscopy study of BeO crystals (Figs. 1–4) were compared in detail with another features earlier known for the intrinsic luminescence

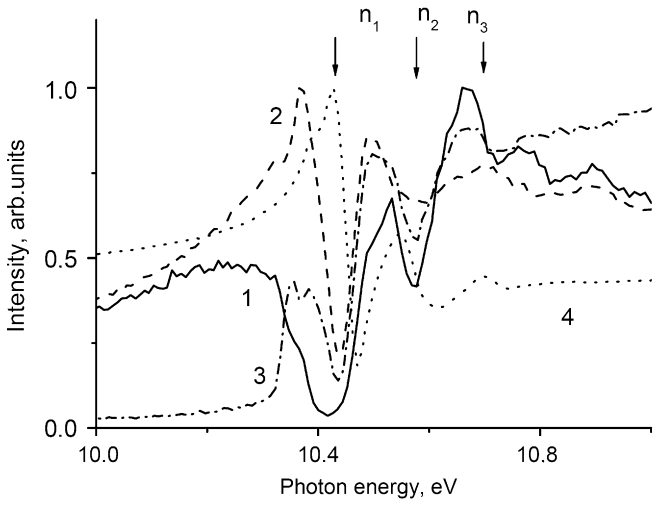

Fig. 2. Excitation spectra of the (1) 3.35 eV luminescence measured in fast ($\Delta t_1 = 2.2$ ns and $\delta t_1 = 8.2$ ns) time window, (2) 4.75 eV and (3) 6.7 eV luminescence measured in slow ($\Delta t_2 = 23$ ns and $\delta t_2 = 111$ ns) time window and (4) reflectivity spectrum of BeO crystals for **E**‖**C** orientation.

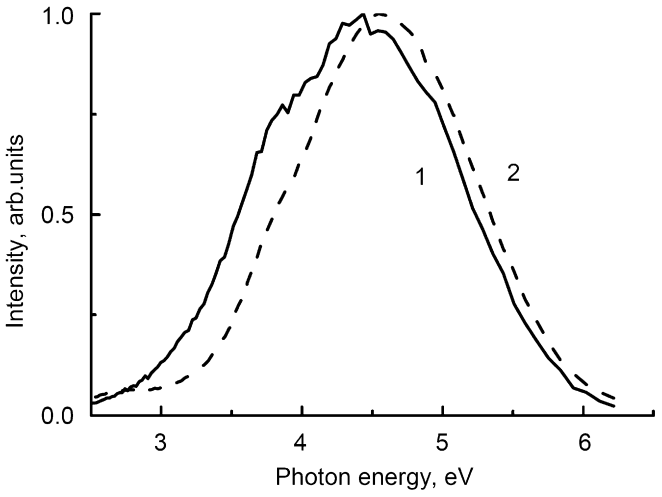

Fig. 3. Time-resolved photoluminescence spectra of BeO crystals ($T = 10$ K) for the crystal orientation **E** ⊥ **C** at the excitation energy of 10.6 eV measured in (1) fast ($\Delta t_1 = 2.2$ ns and $\delta t_1 = 8.2$ ns) and (2) slow ($\Delta t_2 = 23$ ns and $\delta t_2 = 111$ ns) time windows.

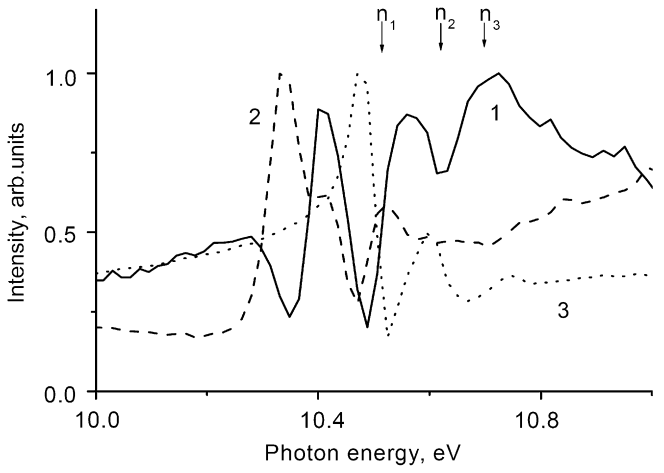

Fig. 4. Excitation spectra of the (1) 4.75 eV and (2) 6.7 eV luminescence measured in slow ($\Delta t_2 = 23$ ns and $\delta t_2 = 111$ ns) time window and (3) reflectivity spectrum of BeO crystals for **E** ⊥ **C** orientation.

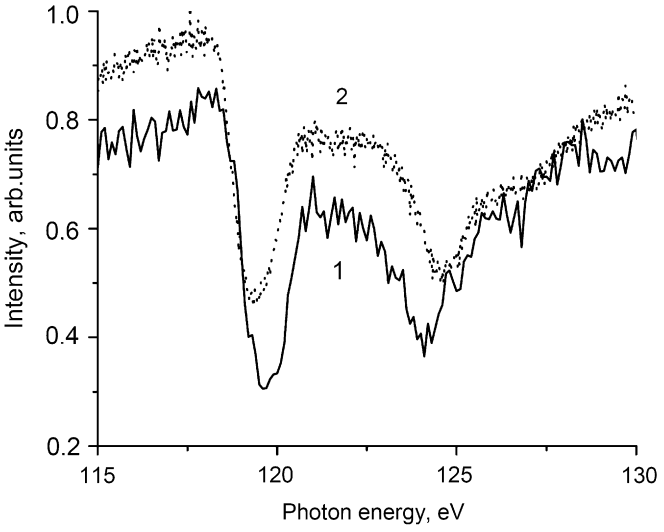

Fig. 5. Luminescence excitation spectra of 4.9 eV emission in BeO crystals for (1) **E**‖**C** and (2) **E** ⊥ **C** orientation at $T = 8$ K. The energy resolution in excitation was 40 (curve 1) and 25 meV (curve 2).

(Pustovarov et al., 2001) and confirmed the model of coexistence of two STE types, which differ in the configuration of a hole nucleus suggested in Ivanov et al. (1994). Pustovarov et al. (2001) developed an idea about multiplicity of the STE excited states. In particular, it was supposed that the fast UV-luminescence (4.0 eV) and VUV-luminescence appear after the radiative decay of the singlet and triplet states of the axial STE1.

Presented in Figs. 1–4 orientational effects in the relaxation paths of the electronic excitations into STE1 or STE2 states were named as "branching" of electronic excitation relaxation. However, Pustovarov et al. (2001) did not discuss the question about the multiplicity of the STE2 excited state because there were found only rather slow decay components (∼ 55 ns) of the UV-luminescence. Such components are typical for the transitions from partially forbidden triplet states. New fast components in the kinetics of the UV-luminescence decay, which can originate from the radiative decay of the singlet STE2 states, were found for the oriented BeO crystal under selective excitation in the range of K-edge absorption of Be. At the selective inner-shell excitation the cation excitons are effectively created.

The excitation spectra of the UV-luminescence for inner-shell excitation in the range of K-edge absorption of Be for the oriented BeO crystals are presented in Fig. 5. New fast component in the UV-luminescence spectra with the maximum at 5.2 eV was obtained at selective excitation by photons with an energy of 119.5 eV only for **E** ⊥ **C** orientation, Fig. 6. The decay time of new component was estimated to be ∼ 1 ns.

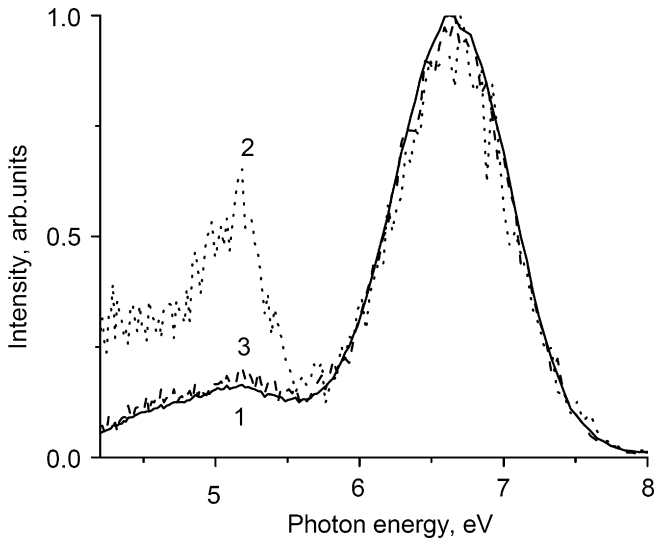

Fig. 6. Luminescence spectra of BeO crystals for **E** ⊥ **C** orientation at $T = 8$ K. $\mathbf{E}_{exc} = 119.5$ eV (1—integral, 2— fast ($\Delta t_1 = 3.4$ ns and $\delta t_1 = 0.2$ ns), 3—slow ($\Delta t_2 = 34$ ns and $\delta t_2 = 118$ ns) time windows).

It was shown earlier that the singlet STE1 excited state was effectively excited by X-ray SR photons or VUV-photons near the fundamental absorption edge (Fig. 1) only at **E**‖**C** orientation. The new fast component of UV-luminescence, being effectively excited at the **E** ⊥ **C** orientation under inner-shell excitation, indicates possible producing the STE2 singlet states.

General question rises that why this fast UV-luminescence was not observed under near fundamental absorption edge excitation at **E** ⊥ **C** orientation. Firstly, an abrupt rise of the absorption coefficient occurs at the Be K-edge. Consequently, the depth of excited crystal range decreases, thereby increasing the density of secondary electronic excitation. On the other hand, Pustovarov et al. (2001) revealed at the **E**‖**C** orientation the fast UV-luminescence with the maximum at 5.0 eV. The nature of this emission was not discussed, whereas its excitation spectrum was located in the narrow edge range near 10.35 eV. Hence, the respective excitation range for the fast component of the UV-luminescence at the **E** ⊥ **C** orientation can be narrow as well.

This requires a dedicated study, which will be carried out soon. The observed at the **E** ⊥ **C** orientation under the selective inner-shell excitation the fast UV-luminescence (5.2 eV) is characterized by a very narrow range of the effective excitation near the K-edge of Be absorption. The possible mechanism of the formation of such excitation is the fast relaxation of the cation exciton with the emitting of X-ray photon and the subsequent formation of the STE2 excited state. Really, Kikas et al. (2005) observed in the oriented BeO crystals the X-ray fluorescence, which is a manifestation of the process of the Be 1s cation exciton relaxation.

Acknowledgments

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